Spin Dynamics of the Magnetoresistive Pyrochlore $Tl_2Mn_2O_7$

J. W. Lynn and L. Vasiliu-Doloc
NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland 20899 and Center for Superconductivity Research, Department of Physics, University of Maryland, College Park, MD 20742

M. A. Subramanian
Dupont Central Research and Development, Experimental Station, Wilmington, DE 19880

Neutron scattering has been used to study the magnetic order and spin dynamics of the colossal magnetoresistive pyrochlore $Tl_2Mn_2O_7$. On cooling from the paramagnetic state, magnetic correlations develop and appear to diverge at T_C $(123K)$. In the ferromagnetic phase well defined spin waves are observed, with a gapless ($\Delta < 0.04$ meV) dispersion relation $E = Dq^2$ as expected for an ideal isotropic ferromagnet. As $T \rightarrow T_C$ from low T, the spin waves renormalize, but no significant central diffusive component to the fluctuation spectrum is observed in stark contrast to the $La_{1-x}(Ca,Ba,Sr)_xMnO_3$ system. These results argue strongly that the mechanism responsible for the magnetoresistive effect has a different origin in these two classes of materials.

PACS numbers: 75.40.Gb, 75.70Pa, 75.30.Kz, 75.25.+z

Pure $LaMnO_3$ is an antiferromagnetic insulator in which the $Mn^{3+}O_3$ octahedra exhibit a Jahn-Teller distortion that strongly couples the magnetic and lattice system [1,2]. Doping with divalent ions such as Ca, Sr, or Ba introduces Mn^{4+}, and with sufficient doping ($x \gtrsim 0.1$) the holes become mobile and the system transforms into a metal. In this metallic regime the double-exchange mechanism allows holes to move only if adjacent spins are parallel, which results in a dramatic increase in the conductivity when the spins order ferromagnetically, either by lowering the temperature or applying a magnetic field. The carrier mobility is thus intimately tied to both the lattice and magnetism, and considerable effort has been devoted to identifying the basic interactions that dominate the energetics and control the magnetoresistive properties. One avenue to unraveling these interactions is by measuring the spin dynamics, and a number of anomalous features have been identified including very strong damping of the spin waves in the ground state [3] and as a function of temperature [4], anomalous spin wave dispersion [5], and the development of a strong spin-diffusion component to the fluctuation spectrum well below T_C [6–8]. Recently a new "colossal" magnetoresistive (CMR) compound has been discovered, namely the pyrochlore $Tl_2Mn_2O_7$ [9,10], and an important question concerns whether this new class of CMR materials contains the same underlying physics, or represents a completely new and different CMR mechanism. We have investigated the magnetic correlations, phase transition, and long wavelength spin dynamics using neutron scattering techniques, and find no evidence of the anomalous spin-diffusion component of the magnetic fluctuation spectrum that dominated the phase transition in the optimally-doped $La_{1-x}Ca_xMnO_3$ (LCMO) manganites and appears to be associated with the spin component of the polaron in these materials. These results, coupled with the absence of any Jahn-Teller effects due to Mn^{3+} in the system [11–13], argues strongly that the Mn pyrochlore belongs to a new class of CMR systems with a different underlying magnetoresistive mechanism.

The neutron scattering measurements were carried out at the NIST Center for Neutron Research. The polycrystalline sample weighed 1.5 g, and the preparation technique, structure, and transport properties are described elsewhere [11,13]. The magnetic diffraction and inelastic data were collected on the BT-9 triple axis spectrometer, with pyrolytic graphite monochromator, analyzer, and filter, and a fixed energy of 13.7 meV. Higher resolution inelastic data close to T_C were taken on the SPINS spectrometer using a fixed final energy of 3.7 meV. Because the long wavelength spin dynamics turns out to be approximately isotropic, inelastic measurements on polycrystalline samples may be made in the forward scattering direction (i.e. around the (000) reciprocal lattice point) without loss in generality [14]. The inelastic measurements were taken with horizontal collimations of 12′-11′-12′-16′ full width at half maximum (FWHM), while for the diffraction data the collimations could be relaxed to improve the data rate. The SANS data were collected on the NG-3 spectrometer using a wavelength of 5 Å and a detector position of 8 m, with the intensity on the two-dimensional position sensitive detector angularly averaged around the beam-center position to obtain $I(|\mathbf{q}|)$. For the present data the experimentally accessible q range is $0.009 \leq q \leq 0.12$ Å^{-1}.

$Tl_2Mn_2O_7$ is cubic ($Fd\overline{3}m$, $a = 9.892$ Å at room tem-

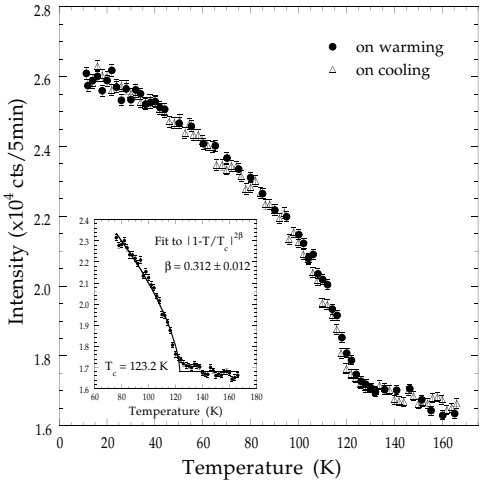

FIG. 1. Intensity of the ferromagnetic Bragg peak vs. temperature. No significant difference is observed on warming and cooling. The inset shows a power law fit, giving T_C=123.2 K and a critical exponent $\beta = 0.312$.

perature), and the temperature dependence of the {111} Bragg peak is shown in Fig. 1. Well above the ferromagnetic ordering temperature the intensity originates from the structural Bragg peak, while the abrupt increase signals the development of long range ferromagnetic order in the sample. There is some additional scattering near T_C due to critical scattering, but for a powder sample this is quite a sharp transition indicative of the high quality and uniformity of the sample. The inset shows a fit of the data to a power law, which yields an estimate for the transition temperature of $T_C = 123.2(3)$ K. The critical exponent we obtain from the fit is $\beta = 0.312(12)$, which is a typical value for a three dimensional ferromagnet. The errors quoted are statistical only. The ordered magnetic moment we observe in the ground state, based on the nuclear and magnetic intensities of the first five Bragg peaks, is $\mu = 2.907(36)\ \mu_B$, which is very close to the 3 μ_B expected for the Mn^{4+} ion. This is a further indication [11,15] that there is no significant concentration of Mn^{3+} in the material, and hence no possibility of the double-exchange mechanism being operative.

The development of magnetic order in this system can also be easily seen in the SANS data, as shown in Fig. 2(a), where the intensity of the scattering for $q = 0.012$ Å^{-1} is shown as a function of temperature. The data in the smallest q regime exhibit an abrupt increase in the scattering at T_C, and we interpret this as scattering due to domains and domain walls. The intensity of this scattering follows the usual Porod form ($I(q) \propto 1/Q^4$) indicating that the size of the objects that are producing the scattering is larger than $2\pi/q \sim 600$ Å. On the other hand, in many ferromagnets this domain scattering is not observable in this q range, which indicates that the size of the domains in $Tl_2Mn_2O_7$ is relatively small.

At larger q the scattering from the domains becomes weak and one can observe the conventional critical scattering, as shown in Fig. 2(b). As the temperature is cooled from above T_C, the scattering increases and peaks near the ordering temperature. Below T_C the scattering originates from spin waves, and this scattering decreases with T due to the decrease in the number of spin waves. The scattering above T_C is found to obey the usual Lorentzian form $I(q) \propto 1/(q^2 + \kappa^2)$, and the correlation length $\xi = 1/\kappa$ is plotted in Fig. 2(c). The range of spin correlations increases as T_C is approached, and appears to diverge at the ordering temperature.

We now turn to the inelastic measurements of the spin fluctuation spectrum. We find that the magnetic system behaves as an ideal isotropic ferromagnet at low T, as is the case for all the metallic ferromagnetic manganites [3–7,16]. The magnetic excitations are conventional spin waves, with a dispersion relation $E = \Delta + D(T)q^2$, where Δ represents the spin wave energy gap and the spin stiffness coefficient $D(T)$ is directly related to the exchange interactions. Fig. 3 shows a typical magnetic inelastic spectrum for a wave vector $q = 0.13$ Å^{-1}. A flat background of 3 counts plus an elastic incoherent nuclear peak of 61 counts, measured at 10 K, have been subtracted from these data. At both temperatures shown we see well defined spin waves in energy gain (E<0) and energy loss (E>0). The solid curve is the result of a least-squares fit of the spin wave cross section, convoluted with the instrumental resolution. At the higher temperature the spin waves have renormalized to lower energy, broadened, and the overall integrated intensity has increased, in agreement with conventional spin wave theory. At each temperature we have taken data at a series of q's, and found that in this hydrodynamic (small q) regime the dispersion obeys a quadratic law within experimental error, with a gap that is too small to determine ($\Delta < 0.04$ meV). Thus we conclude that $Tl_2Mn_2O_7$ behaves as a "soft" isotropic ferromagnet to an excellent approximation.

The temperature dependence of the spin wave stiffness parameter $D(T)$ is shown in Fig. 4. In the ground state we obtain a value of $D = 39(1)$ meV·Å^2. The ratio of $D(0)/k_BT_C = 3.67$ Å^2 gives an estimate of the range of the exchange interaction, and this result indicates that nearest neighbor interactions dominate the energetics. At elevated temperatures we find that the spin waves soften, and appear to collapse as $T \to T_C$; the data taken at 125 K exhibit spin diffusion, with a spin-diffusion coefficient $\Lambda = 11.5(8)$ meV·Å^2. This behavior is in stark contrast to the behavior of the Ca-doped CMR materials, where a quasielastic spin diffusion component develops as the Curie temperature is approached, and in the range of optimal doping dominates the fluctuation spectrum. In the LCMO case the spin waves do not appear to renormalize to zero, and hence the ferromagnetic transition is not driven by the usual route of the thermal

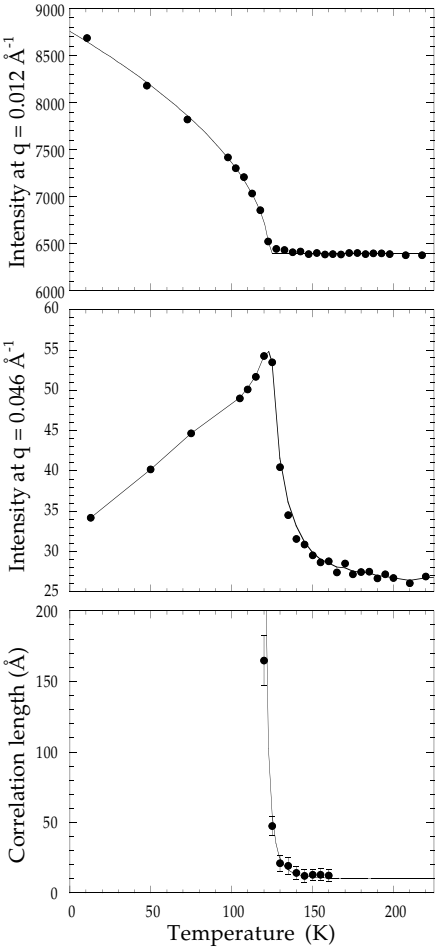

FIG. 2. Temperature dependence of the energy-integrated small angle magnetic scattering (a) at small q, where the scattering is dominated by domain wall scattering and thus follows a power of the magnetization (solid curve), (b) at larger q, where the usual critical scattering in the vicinity of the Curie temperature is observed. The solid curve is a guide only. (c) the temperature dependence of the spin correlation length, showing that it rises rapidly with decreasing temperature and appears to diverge at T_C. The solid curve is a fit to a power law.

population of conventional spin waves. Rather, the ferromagnetic phase transition appears to be driven by the quasielastic component, which has been identified as the spin component of the polaron in this system [17]. A central component to the fluctuation spectrum has also been observed in the Sr doped [8] and Ba doped materials [18], as well as for $Nd_{0.7}Sr_{0.3}MnO_3$ and $Pr_{0.7}Sr_{0.3}MnO_3$ [7]. In this latter work the authors suggested that the strength of the central peak is inversely related to the value of T_C, and with the low value of T_C of 123K for $Tl_2Mn_2O_7$ one would then expect strong quasielastic scattering if the physics were the same for these two classes of materials. The data in Fig. 3 clearly show that we find *no* evidence for a quasielastic component to the fluctuation spectrum in the present material. There might still be a central component to the fluctuation spectrum at smaller q or for temperatures closer to T_C than have been investigated here, but it is clear that the spin dynamics in the pyrochlore is fundamentally different than in the doped manganites.

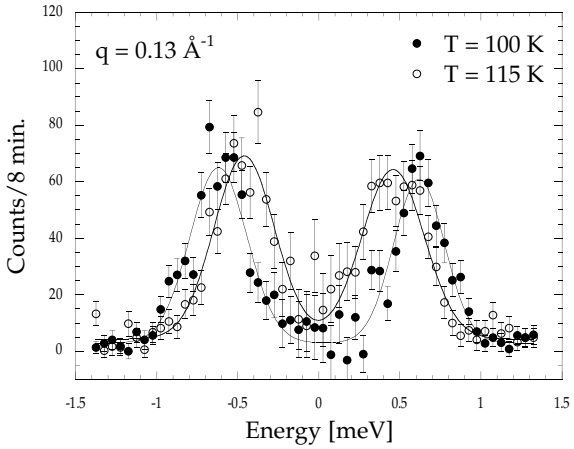

FIG. 3. Inelastic spectrum at $q = 0.13$ Å^{-1} for two temperatures below T_C. Spin waves are observed in energy gain ($E < 0$) and energy loss ($E > 0$). The solid curves are fits to a double Lorentzian spectral weight function convoluted with the instrumental resolution. With increasing T the spin waves are seen to renormalize to lower energy, broaden, and increase in intensity, as expected. No central component of the fluctuation spectrum is observed, in strong contrast to the behavior of the $La_{1-x}A_xMnO_3$ systems.

The behavior for $Tl_2Mn_2O_7$ contrasts with that observed for the doped $LaMnO_3$ manganite materials in the following important ways: i) in the present system there is no evidence, from a variety of different experimental techniques, of any significant Mn^{3+} or associated mixed-valent behavior, ii) there is also no significant structural distortion that accompanies the development of a bulk magnetization, either as a function of decreasing temperature or increasing applied magnetic field, iii) the magnetic correlation length appears to grow and diverge at T_C in the pyrochlore, while in the Ca-doped manganite the correlation length is short (∼12 Å) and only weakly temperature dependent [6,19], iv) for the spin dynamics, $D(T)$ appears to collapse as the Curie temperature is approached from below, while for LCMO the spin wave energies remain finite, and the phase transition appears to be controlled by the development of a spin-diffusion central component to the fluctuation spectrum. These results taken together argue convincingly that the large magnetoresistance in the pyrochlore has a different origin than in the manganites. In particular, band structure calculations [20] suggest that for $Tl_2Mn_2O_7$ the conductivity comes predominantly from a Tl-O band rather than from the manganese lattice, and hence the magnetic behavior and conduction arise from different sublattices.

However, the conduction bands turn out to be strongly spin differentiated in the ferromagnetic state (as they are in the manganites) and this is thought to produce the particularly strong spin scattering of the conduction electrons that is responsible for the CMR effect. This separation of the ferromagnetic lattice and the conduction band has been clearly revealed in recent doping studies, where the resistivity and CMR was varied by orders-of-magnitude with Sc substitution on the Tl site, while the magnetic properties changed only modestly [15]. With the very small conduction electron density n found in the pyrochlore [9,11], a model based on these observations has recently been developed, as a low-density electron gas coupled to ferromagnetic spin fluctuations [21]. This model predicts a spin polaron regime, but only sufficiently above T_C (when $n \lesssim \kappa^3$), and a delocalization to an itinerant regime occurs due to the growth of ferromagnetic correlations as T_C is approached. The data of Fig. 2(c) suggest that this crossover probably occurs quite close to T_C. Below T_C significant spin polaron effects would not be expected in this theory, in agreement with our observations. Direct observation of the proposed spin polarons above T_C will be quite difficult, though, because the strong spin-diffusion scattering associated with the conventional paramagnetic scattering will mask the small intensity associated with the low carrier density. Single crystal samples will likely be necessary to explore this possibility.

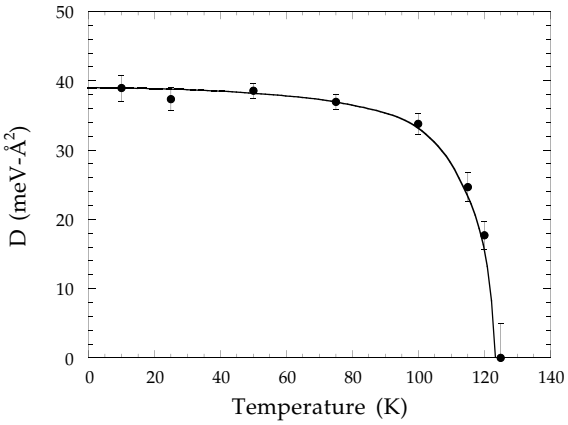

FIG. 4. Temperature dependence of the spin wave stiffness $D(T)$, showing that the spin waves renormalize in the usual way as the ferromagnetic transition is approached. The solid curve is a guide only.

Research at the University of Maryland is supported by the NSF, DMR 97-01339 and NSF-MRSEC, DMR 96-32521. SPINS is supported in part by NSF, DMR 94-23101.

[1] For references to some of the earlier literature see, for example, G. H. Jonker and J. H. Van Santen, Physica **16**, 337 (1950); *ibid* **19,** 120 (1950); E. O. Wollan and W. C. Koehler, Phys. Rev. **100**, 545 (1955); C. Zener, Phys. Rev. **81**, 440 (1951), *ibid* **82**, 403 (1951); J. B. Goodenough, Phys. Rev. **100**, 564 (1955); P. W. Anderson and H. Hasegawa, Phys. Rev. **100**, 675 (1955).

[2] A.J. Millis, P.B. Littlewood, and B.I. Shraiman, Phys. Rev. Lett. **74**, 5144 (1995); A.J. Millis, Phys. Rev. B **55**, 6405 (1997).

[3] L. Vasiliu-Doloc, J. W. Lynn, A. H. Moudden, A. M. de Leon-Guevara, and A. Revcolevschi (preprint)

[4] T. G. Perring, G. Aeppli, S. M. Hayden, S. A. Carter, J. P. Remeika, and S-W. Cheong, Phys. Rev. Lett. **77**, 711 (1996).

[5] H. Y. Hwang, P. Dai, S-W. Cheong, G. Aeppli, D. A. Tennant, and H. A. Mook, Phys. Rev. Lett. **80**, 1316 (1998).

[6] J. W. Lynn, R. W. Erwin, J. A. Borchers, Q. Huang, A. Santoro, J. L. Peng, and Z. Y. Li, Phys. Rev. Lett. **76**, 4046 (1996).

[7] J. A. Fernandez-Baca, P. Dai, H. Y. Hwang, S-W. Cheong, and C. Kloc, Phys. Rev. Lett. **80**, 4012 (1998).

[8] L. Vasiliu-Doloc, J. W. Lynn, Y. M. Mukovskii, A. A. Arsenov, and D. A. Shulyatev, J. Appl. Phys. **83** (1998) (in press).

[9] Y. Shimakawa, Y. Kubo, and T. Manako, Nature **379**, 53 (1996).

[10] For a review of the pyrochlores, see M. A. Subramanian and A. W. Sleight, Chapter 107 in *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 16, Ed. by K. A. Geschneider, Jr. and L. Eyring (Elsevier, New York 1993).

[11] M. A. Subramanian, B. H. Toby, A. P. Ramirez, W. J. Marshall, A. W. Sleight, and G. H. Kwei, Science **273**, 81 (1996).

[12] Y. Shimakawa, Y. Kubo, T. Manako, Y. V. Sushko, D. N. Argyriou, and J. D. Jorgensen, Phys. Rev. B **55**, 6399 (1997)

[13] G. H. Kwei, C. H. Booth, F. Bridges, and M. A. Subramanian, Phys. Rev. B **55**, R688 (1997).

[14] For a recent review of the experimental technique see J. W. Lynn and J. A. Fernandez-Baca, Chapter 5 in *The Magnetism of Amorphous Metals and Alloys*, ed. by J. A. Fernandez-Baca and W-Y. Ching (World Scientific, New Jersey (1995), p. 221.

[15] A. P. Ramirez and M. A. Subramanian, Science **277**, 546 (1997).

[16] M. C. Martin, G. Shirane, Y. Endoh, K. Hirota, Y. Moritomo, and Y. Tokura, Phys. Rev. B **53**, 14285 (1996).

[17] J. W. Lynn, R. W. Erwin, J. A. Borchers, Q. Huang, A. Santoro, J. L. Peng, and R. L. Greene, J. Appl. Phys. **81**, 5488 (1997).

[18] J. W. Lynn, L. Vasiliu-Doloc, S. Skanthakumar, S. N. Barilo, G. L. Bychkov, and L. A. Kurnevitch (preprint).

[19] J. M. De Teresa, M. R. Ibarra, P. A. Algarabel, C. Ritter, C. Marquina, J. Blasco, J. Garcia, A. del Moral, and Z.Arnold, Nature **386**, 256 (1997).

[20] D. J. Singh, Phys. Rev. B **55**, 313 (1997).

[21] P. Majumdar and P. Littlewood (preprint).